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translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

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2. That I am well acquainted with the French and English languages.

3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in France on 6 April 1999 under the number 99/04,262 and the official certificate attached hereto.

4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc

The 20th day of May 2003

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I hereby certify that this paper is being facsimile transmitted to the Commissioner of Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on the date shown below.

Name: James E Boland Reg No. 31,432

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Date: June 19, 2003

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PATENT

UTILITY CERTIFICATE - CERTIFICATE OF ADDITION

OFFICIAL COPY

The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, 17 FEB. 2000

On behalf of the Director-General of the
Institut National de la Propriété Industrielle
The Patent Department Head

(signature)
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PATENT, UTILITY CERTIFICATE

Intellectual Property Code - Book VI

REQUEST FOR GRANT

Confirmation of filing by fax ☐

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Reserved for the INPI	
DATE OF SUBMISSION OF THE DOCUMENTS	06 APR 1999
NATIONAL REGISTRATION	99/04,262
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1. NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM THE CORRESPONDENCE IS TO BE ADDRESSED

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No of permanent power of attorney	Correspondent's reference	Telephone
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2. APPLICATION — Nature of the industrial property right

☒ patent ☐ divisional application ☐ initial application ↓ ☐ patent

☐ utility certificate ☐ conversion of a European patent application ☐ utility certificate No. Date

Compilation of the search report ☐ deferred ☒ immediate

The applicant, as a physical person, asks to pay the fee by instalments ☐ yes ☒ no

Title of the invention (maximum 200 characters)

COEXTRUSION BINDER, ITS USE FOR A MULTILAYER STRUCTURE AND THE STRUCTURE THUS OBTAINED.

3 APPLICANT(S) SIREN No. APE-NAF code

name and forenames (underline the surname) or company name

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If insufficient space, continue on plain paper ☐

4 INVENTOR(S) The inventors are the applicants ☐ yes ☒ no If the answer is no, provide a separate designation

5. REDUCTION OF THE RATE OF FEES ☐ requested for the first time ☐ requested prior to filing, attach copy of the favourable decision

6 PRIORITY DECLARATION OR APPLICATION FOR THE BENEFIT OF THE FILING DATE OF A PRIOR APPLICATION

Country of origin	Number	Filing date	Nature of the application

7 DIVISIONS previous to the present application

No.	date	No	date

8. SIGNATURE OF THE APPLICANT OR REPRESENTATIVE (name and capacity of the signatory - registration No.)

[signature]

SIGNATURE OF THE RECEIVING OFFICIAL

SIGNATURE AFTER REGISTRATION OF THE APPLICATION AT THE INPI

[illegible signature]

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PATENT, UTILITY CERTIFICATE

DESIGNATION OF THE INVENTOR
(if the applicant is not the inventor or the sole inventor)

HN/fo
AM 1449

NATIONAL REGISTRATION NO.
99/04,262

PATENTS ADMINISTRATIVE DIVISION

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TITLE OF THE INVENTION:

COEXTRUSION BINDER, ITS USE FOR A MULTILAYER STRUCTURE AND THE STRUCTURE THUS OBTAINED.

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NOTE: In exceptional cases, the name of the inventor may be followed by that of the company to which he belongs (membership company) when the latter is other than the company which is the applicant or proprietor.

Date and signature(s) of the applicant(s) or of the representative

6 April 1999

Henry NEEL *[signature]*

COEXTRUSION BINDER, ITS USE FOR A MULTILAYER STRUCTURE AND THE STRUCTURE THUS OBTAINED

The present invention relates to a coextrusion binder, to its use for making a multilayer structure and to the structure thus obtained.

More specifically, the coextrusion binder of the present invention comprises:

- 5 to 30 parts of a polymer (A), itself comprising a blend of a polyethylene (A1) of density between 0.935 and 0.980 and of a polymer (A2) chosen from elastomers, very low-density polyethylenes and ethylene copolymers, the (A1) + (A2) blend being cografted with an unsaturated carboxylic acid;
- 95 to 70 parts of a polyethylene (B) of density between 0.930 and 0.950;
- the blend of (A) and (B) being such that:
  - its density is between 0.930 and 0.950,
  - the content of grafted unsaturated carboxylic acid is between 30 and 10,000 ppm,
  - the MFI (melt flow index) measured according to ASTM D 1238 at 190°C/21.6 kg is between 5 and 100.

The present invention also relates to a multilayer structure comprising a layer which comprises the coextrusion binder defined above and, directly attached to the latter, a layer (E) of a nitrogen-containing or oxygen-containing polar resin, such as a layer of a polyamide resin, of an aliphatic polyketone, of a saponified ethylene-vinyl acetate copolymer (EVOH) or of a polyester resin, or else a metal layer.

The invention also relates to a structure comprising the above structure and, directly attached to the latter on the binder side, either a polyolefin layer (F) or a layer of a resin chosen from the resins of the layer (E), or else a metal layer.

The invention also relates to a structure comprising, respectively, a polyolefin layer (F), a layer of the binder defined above, a layer of a of a saponified ethylene-vinyl

acetate copolymer (EVOH), a layer of the binder defined above and a polyolefin layer (F).

These structures are useful for manufacturing flexible or rigid packages, such as sachets, bottles or containers. These packages may be manufactured by coextrusion, lamination or coextrusion-blow moulding.

The invention is useful in particular for coextruded hoses or pipes and for motor-vehicle petrol tanks.

Petrol tanks usually consist of five layers consisting respectively of:

- high-density polyethylene (HDPE);
- a binder;
- a polyamide (PA) or a copolymer having ethylene units and vinyl alcohol units (EVOH);
- a binder;
- HDPE.

Very often, a sixth layer is added between one of the binder layers and one of the HDPE layers. This sixth layer consists of manufacturing scrap resulting from the moulding of the tanks or, for a much smaller quantity, tanks which are off-specification. This scrap and these off-specification tanks are ground up in order to obtain granules. This regrind is then remelted and extruded directly on the plant for coextruding the tanks. This regrind could also be melted and regranulated by an extrusion machine, such as a twin-screw extruder, before it is reused.

According to a variant, the recycled product may be blended with the HDPE of the two outermost layers of the tank. It is also possible, for example, to blend the granules of recycled product with the virgin HDPE granules of these two layers. Any combination of these recycling operations may also be used.

The amount of recycled material may represent up to 50% of the total weight of the tank.

This sixth layer therefore includes all the multilayer structure, namely HDPE.

binders, PA or EVOH.

The prior art has already described multilayer petrol tanks. EP 834,415 describes structures comprising:

polyethylene/binder/EVOH/binder/polyethylene.

The binder is a maleic-anhydride-grafted polyethylene having an MFI of 0.1 to 3 and a density between 0.920 and 0.930 and it contains 2 to 40% by weight of material insoluble in n-decane at 90°C.. It is explained that the grafted polyethylene is dissolved in n-decane at 140°C and cooled to 90°C, products precipitate; it is then filtered and the insoluble content is the percentage by weight which precipitates and is collected by filtration at 90°C.

If the content is between 2 and 40%, the binder has good petrol resistance.

No example shows such a polymer. The text specifies that the binder is in fact a blend of 2 to 30 parts of a grafted polyethylene having a density between 0.930 and 0.980 and of 70 to 98 parts of an ungrafted polyethylene having a density between 0.910 and 0.940, preferably 0.915 and 0.935.

The Applicant has tried to prepare binders and the corresponding structures in accordance with this teaching. It has found that the binders were not reproducible, that is to say the choice of the product by its density is not a sufficient indication. The Applicant has also found that these criteria were not sufficient for the binder to withstand petrol.

The invention will now be described in detail.

With regard to the polymer (A1), this is a polyethylene homopolymer or a copolymer of ethylene with a comonomer chosen, for example, from:

- α-olefins, advantageously those having from 3 to 30 carbon atoms. Examples of α-olefins having 3 to 30 carbon atoms as possible comonomers comprise propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-dodecene, 1-tetradecene,

1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1-octacocene and 1-triacontene. These α-olefins may be used by themselves or as a blend of two or more of them;

- the esters of unsaturated carboxylic acids, such as, for example, alkyl (meth)acrylates, the alkyl of which has from 1 to 24 carbon atoms. Examples of alkyl acrylates or methacrylates that can be used are, in particular, methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;

- the vinyl esters of saturated carboxylic acids, such as, for example, vinyl acetate or vinyl propionate.

Advantageously, (A1) is a high-density polyethylene (HDPE) of density between 0.940 and 0.965.

The MFI of (A1) is between 0.1 and 3 at 2.16 kg.

The copolymer (A2) may, for example, be an ethylene/propylene elastomer (EPR) or an ethylene/propylene/diene elastomer (EPDM).

(A2) may also be a very low-density polyethylene (VLDPE) which is either an ethylene homopolymer or an ethylene/α-olefin copolymer.

(A2) may also be a copolymer of ethylene with at least one product chosen from (i) unsaturated carboxylic acids, their salts and their esters, (ii) vinyl esters of saturated carboxylic acids and (iii) unsaturated dicarboxylic acids, their salts, their esters, their half-esters and their anhydrides.

(A2) may be a metallocene polyethylene.

The amounts of (A1) and (A2) are advantageously 60 to 95 parts of (A1) for 40 to 5 parts of (A2).

The blend of (A1) and (A2) is grafted with an unsaturated carboxylic acid, that is to say (A1) and (A2) are cografted. It would not be outside the scope of the invention to use a functional derivative of this acid.

 unsaturated carboxylic acids are

those having 2 to 20 carbon atoms, such as acrylic, methacrylic, maleic, fumaric and itaconic acids. The functional derivatives of these acids comprise, for example, anhydrides, ester derivatives, amide derivatives, imide derivatives and metal salts (such as alkali metal salts) of unsaturated carboxylic acids.

Unsaturated dicarboxylic acids having 4 to 10 carbon atoms and their functional derivatives, particularly their anhydrides, are particularly preferred grafting monomers.

These grafting monomers comprise, for example, maleic, fumaric, itaconic, citraconic, allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylcyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic and x-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids and maleic, itaconic, citraconic, allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic and x-methyl-bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic anhydrides.

Examples of other grafting monomers comprise C_1-C_8 alkyl esters or glycidyl ester derivatives of unsaturated carboxylic acids, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, monoethyl maleate, diethyl maleate, monoethyl fumarate, dimethyl fumarate, monomethyl itaconate and diethyl itaconate; amide derivatives of unsaturated carboxylic acids, such as acrylamide, methacrylamide, the monoamide of maleic acid, the diamide of maleic acid, the N-monoethylamide of maleic acid, the N,N-diethylamide of maleic acid, the N-monobutylamide of maleic acid, the N,N-dibutylamide of maleic acid, the monoamide of furamic [sic] acid, the diamide of furamic [sic] acid, the N-mono-ethylamide of fumaric acid, the N,N-diethylamide of fumaric acid, the N-monobutylamide of fumaric acid and the N,N-dibutylamide of fumaric

 atives of unsaturated carboxylic

acids, such as maleimide, N-butylmaleimide, N-phenylmaleimide; and metal salts of unsaturated carboxylic acids, such as sodium acrylate, sodium methacrylate, potassium acrylate and potassium methacrylate. Maleic anhydride is preferred.

Various known processes may be used to graft a grafting monomer onto the blend of (A1) and (A2).

For example, this may be carried out by heating the polymers (A1) and (A2) to high temperatures, approximately 150 to approximately 300°C, in the presence or absence of a solvent and with or without a radical initiator. Suitable solvents that may be used in this reaction are benzene, toluene, xylene, chlorobenzene, cumene, etc. Suitable radical initiators which can be used comprise *tert*-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, di-*tert*-butyl peroxide, *tert*-butylcumyl peroxide, dicumyl peroxide, 1,3-bis(*tert*-butylperoxyisopropyl)-benzene, acetyl peroxide, benzoyl peroxide, isobutyryl peroxide, bis(3,5,5-trimethylhexanoyl) peroxide and methyl ethyl ketone peroxide.

The amount of grafting monomer in the blend of (A1) and (A2) modified by the grafting obtained in the abovementioned manner may be chosen in an appropriate manner, but it is preferably 0.01 to 10%, better still 600 ppm to 6%, with respect to the weight of grafted (A1) and (A2).

The amount of grafted monomer is determined by assaying the succinic functional groups by FTIR spectroscopy.

The MFI of (A), that is to say of (A1) and (A2) which have been cografted, is 5 to 100/21.6 kg. As regards the polyethylene (B), this is a homopolymer or copolymer polyethylene [sic].

The density of (B) is advantageously between 0.930 and 0.940.

The MFI of (B): 5 to 100/21.6 kg.

According to one advantageous form of the

er comprises 5 to 20 parts of (A)

per 95 to 80 parts of (B).

The density of the blend (A) + (B) is advantageously between 0.930 and 0.940.

The multilayer structure of the present invention consists of the layer comprising the above binder and of a layer (E) of oxygen-containing or nitrogen-containing polar resin, or a metal layer.

Examples of preferred polar resins in the layer other than the binder are polyamide resins, an aliphatic polyketone, a saponified ethylene-vinyl acetate copolymer and polyesters.

More specifically, they comprise long-chain synthetic polyamides having structural units of the amide group in the main chain, such as PA-6, PA-6,6, PA-6,10, PA-11, PA-6/6,6 and PA-12; a saponified ethylene-vinyl acetate copolymer having a degree of saponification of approximately 90 to 100 mol%, obtained by saponifying an ethylene/vinyl acetate copolymer having an ethylene content of approximately 15 to 60 mol%; polyesters such as polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthenate, blends of these resins, or else aromatic polyesters such as liquid-crystal polymers.

The metal layer may, for example, be a sheet, a film or a foil of a metal such as aluminium, iron, copper, tin and nickel or an alloy containing at least one of these metals as the main constituent. The thickness of the film or of the foil may be suitably chosen and is, for example, approximately 0.01 to approximately 0.2 mm. It is common practice to degrease the surface of the metal layer before laminating the binder of the invention to it. The layer of oxygen-containing or nitrogen-containing polar resin (E) may also contain known additives in conventional amounts.

The invention also relates to a structure comprising respectively a polyolefin layer (F), a layer of the binder of the invention and either a layer (E) of oxygen-containing or nitrogen-containing polar resin

or a metal layer. According to another particular embodiment, the invention relates to a structure respectively comprising an HDPE layer, a layer of the binder of the invention, a layer of EVOH (or of an EVOH alloy) or a layer of polyamide (or based on polyamide), a layer of the binder of the invention and an HDPE layer. Advantageously, it is in the form of rigid hollow bodies having a volume of 0.1 to 200 litres. The total thickness is between 0.2 and 20 mm, the EVOH or the polyamide representing 0.5 to 15% of this thickness, each binder layer 0.2 to 10% and the two HDPE layers the balance.

The MFI of the HDPE is preferably 3 to 17 g/10 min. at 190°C/21.6 kg.

The MFI of the EVOH is preferably 1 to 10 g/10 min. at 190°C/2.16 kg.

Advantageously, the external layer of HDPE may be replaced by two layers, the outer one made of optionally coloured virgin HDPE and the other made of recycled product coming from scrap and cuttings from the extrusion-blow moulding of these hollow bodies. The thickness of the external HDPE layer added to the thickness of the layer of recycled material is essentially the same as in the case of a single HDPE external layer.

These structures are useful for making petrol tanks or tubings for filling petrol tanks.

The various layers of the structures of the invention may contain additives such as fillers, stabilizers, slip agents, antistatic agents and fire-retardants.

The structures of the invention may be manufactured by coextrusion and extrusion-blow moulding processes, known in the field of thermoplastics.

Examples

The examples presented correspond to 5-layer structures from bottles produced by extrusion-blow moulding under the following conditions.

Structure of the bottle:

- 3 constituents, 5 layers;
- HDPE/binder/EVOH/binder/HDPE;
- thicknesses: 1.2/0.1/0.15 (EVOH) to 0.25 (PA)/0.1/1.2 mm;
- HDPE: density = 0.945 - 0.950 and MFI = 5 - 6 g/10 min. (190°C/21.6 kg);
- EVOH: ethylene content = 29% MFI = 1.7 g/10 min. (190°C/2.16 kg).
- POLYMIDE: copolyamide 6/6,6 such as the ULTRAMID C4FN from BASF.

Type of bottle:

Cylinder (Ø = 70 mm) with 2 plane faces, 0.7 litre, height = 270 mm and weight = 170 g.

Extrusion-blow moulding conditions

Temperature profiles (°C):

						Head
HDPE	200	210	220	230	230	230
Binder	210	220	220	220	220	230
EVOH	180	190	200	210	220	230

Tooling Diameter of the die = 20 mm
Diameter of the mandrel = 12 mm
Gap = 4 mm

Blowing stretch ratio: approximately 3.

Measurement of the interlayer peel strength

- 15 × 150 mm test-pieces cut from the plane parts of the bottle and conditioned for at least 24 hours at 23°C and 50% RH;
- cutter initiation at one of the binder/EVOH or binder/polyamide interfaces;
- "T" peel test at a crosshead speed of 50 mm/min. The peel strength, expressed in N/cm, is given by the plateau value of the peel force, excluding the starting peak. "MA" denotes maleic anhydride and the weight % of the cografted blend (A) denotes the proportion of the blend A in A + B.

Table 1

Formulations		Example 1	Example 2	Example 3
Polymer A1	Density (g/cm^3)	0.958	0.940	0.950
	MFI (g/10 min./2.16 kg)	0.9	1	1
	% by weight	80	75	90
Polymer A2	Comonomer	propylene	1-octene	propylene
	Density (g/cm^3)	0.880	0.870	0.880
	MFI (g/10 min./2.16 kg)	0.2	5	0.2
	% by weight	20	25	10
Cografted blend A	MA content (ppm)	4000	10000	6000
	% by weight	20	25	10
Polymer B	Density (g/cm^3)	0.934	0.938	0.936
	MFI (g/10 min./21.6 kg)	14	20	18
A + B blend	Density (g/cm^3)	0.936	0.934	0.937
	MFI (g/10 min./21.6 kg)	15	18	18
	MA content (ppm)	800	2500	600
Peel strength	On PA 6/6,6 (N/cm)	70	80	75
	On EVOH	50	55	55

CLAIMS

1. Coextrusion binder comprising:

- 5 to 30 parts of a polymer (A), itself comprising a blend of a polyethylene (A1) of density between 0.935 and 0.980 and of a polymer (A2) chosen from elastomers, very low-density polyethylenes and ethylene copolymers, the (A1) + (A2) blend being cografted with an unsaturated carboxylic acid;

- 95 to 70 parts of a polyethylene (B) of density between 0.930 and 0.950;

- the blend of (A) and (B) being such that:

. its density is between 0.930 and 0.950,

. the content of grafted unsaturated carboxylic acid is between 30 and 10,000 ppm,

. the MFI (melt flow index) measured according to ASTM D 1238 at 190°C/21.6 kg is between 5 and 100.

2. Binder according to Claim 1, in which the density of (A) + (B) is between 0.930 and 0.940.

3. Multilayer structure comprising a layer comprising the binder of any one of the preceding claims and, directly attached to the latter, a layer (E) of nitrogen-containing or oxygen-containing polar resin, such as a layer of polyamide resin, of an aliphatic polyketone, of a saponified ethylene-vinyl acetate copolymer (EVOH) or of a polyester resin, or else a metal layer.

4. Structure according to Claim 3, in which either a polyolefin layer (F) or a layer of a resin chosen from the resins of the layer (E) or a metal layer is directly attached on the binder side.

5. Structure according to Claim 4, respectively comprising an HDPE layer, a layer of the binder of the invention, either a layer of EVOH or of an EVOH alloy or a polyamide or polyamide-based layer, a layer of the binder of the invention and an HDPE layer.

6. Rigid hollow bodies consisting of a structure of Claims 3 to 5.

7. Petrol tank comprising a structure according to Claim 5.